

DIELECTRIC CONSTANT STUDIES

V. Anomalous Dispersion of Lecithin in Viscous
Mineral Oils

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the University of Michigan

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V. Anomalous Dispersion of Lecithin in Viscous Mineral Oils

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A unique receiver and accompanying cell for determining dielectric constants by the resonance method were constructed. Their design is such as to reduce to a minimum several types of error inherent in the resonance method. Dielectric constant measurements were made on five solutions of lecithin in very viscous mineral oils at three temperatures and at six wavelengths. Three distinct methods were employed: (1) refractometer method—frequency of D line of sodium, (2) resonance method—32.8 m, 94 m, 320 m, 1308 m, (3) bridge method—precision Wheatstone

bridge, 1036 cycles. Analyses of the experimental curves and comparisons with theoretical Debye curves definitely indicate dispersion though not of a simple type. Another series of measurements made on one solution at 16 different wavelengths covering the range from 40 m to 5,000,000 m still failed to show any individual simple dispersion regions. A qualitative explanation based on varying viscosities of the components of the solvent, the presence of polar radicals in the solute molecules, and the extensive association of the solute is offered.

EVIDENCE is becoming more convincing that the viscosity affecting the rotation of dipole molecules in an alternating field, referred to as microscopic viscosity, is not the same as that measured by the ordinary method, known as macroscopic viscosity.

The determination of microscopic viscosity by means of dielectric constant measurements is based upon the theoretical work of Debye on anomalous dispersion, the decrease in dielectric constant with increasing frequency. A large ab-

sorption of energy occurs simultaneously with anomalous dispersion.

In an alternating electric field four things increasingly oppose the turning of molecular dipoles. These are: Increasing viscosity, increasing particle size, increasing frequency, and decreasing temperature, the last due largely to its effect on the viscosity.

The effect of these factors is to throw the orientation of the molecules out of phase with the applied field. It is this lagging of the molecules behind the field that causes the great absorption of energy in the region of anomalous dispersion.

* Rewritten from a thesis by G. Harlowe Evans in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

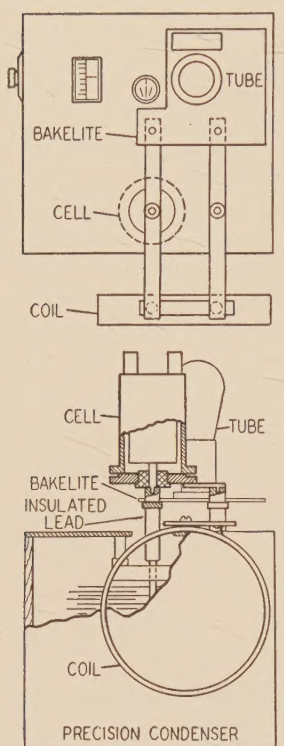


FIG. 1. Cell and receiver assembly.

It thus appears that by measurements of dielectric constants in the region of anomalous dispersion one should be able to measure the viscosity which is really involved in the turning of the dipole molecules.

Measurements of this kind are reported in the literature for extremely large molecules of uncertain molecular weight in fairly fluid solvents^{1, 2, 3} and also for small well-defined molecules in very viscous solvents.^{4, 5} However, no information seems to be available on systems of molecules of large but definite molecular weight in solvents of moderately high viscosities. It was the original purpose of this investigation to study the relation between microscopic and macroscopic viscosity in such a system.

Solutions of lecithin (molecular weight 804) in Sun Oils S. A. E. 30, 40, 50, and 60 were found to possess the required characteristics. These oils

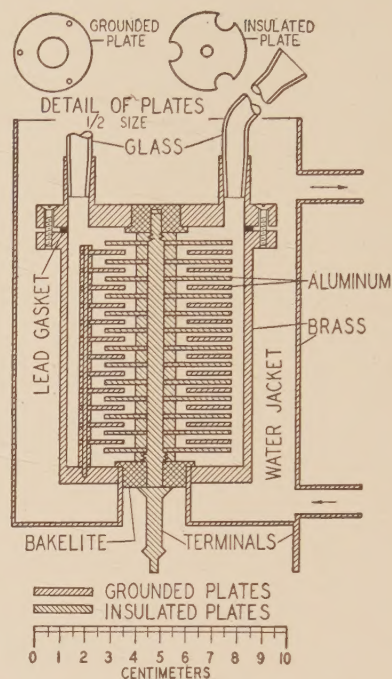


FIG. 2. The dielectric constant cell No. 3.

are unusually pure and cover the viscosity range from 3.66 to 21.5 poises at 25°C. For Sun Oils 30, 40 and 60, 10 percent solutions were used, while for Sun Oil 50 two solutions containing 3 percent and 10 percent were employed.

With these solutions dielectric constants were measured at six frequencies and at three temperatures. The results allow a study of the influence of viscosity, temperature and concentration on the dielectric constant.

The values of ϵ_0 (the dielectric constant at optical frequencies) were obtained from refractive indices measured by means of an Abbe refractometer, making use of the Maxwellian relation $n^2 = \epsilon$ where n is the refractive index. Assuming that 300,000 meters (1000 cycles) is a long enough wavelength, values of ϵ_∞ (the so-called "static" dielectric constant) were determined at this wavelength by means of a precision Wheatstone bridge assembly developed by Mr. R. D. Thompson in this laboratory.

The values of ϵ' (the measured dielectric constant) at wavelengths of 32.8 m, 94 m, 320 m, 1308 m were calculated from capacitance measurements made by the substitution method employing a simple "voltage tuning" resonance apparatus very similar in electrical arrangement to

¹ J. Wyman, Jr., *J. Biol. Chem.* **90**, 443 (1931).

² N. Marinesco, *J. chim. phys.* **27**, 454 (1930); **28**, 51 (1931); *Comptes rendus* **192**, 625 (1931).

³ J. Errera, *J. chim. phys.* **29**, 577 (1932).

⁴ Goldammer-Sack, *Physik. Zeits.* **31**, 224 (1930).

⁵ R. Luthi, *Helv. Phys. Acta* **6**, 139 (1933).

one used previously by Malone^{6,7} in this laboratory. Malone found this to be the most suitable method of determining the dielectric constants of small amounts of liquids over a wide range of wavelengths.

For the voltage-tuning resonance method at high frequencies, Lattey⁸ has summarized the sources of error which should be eliminated or for which corrections should be made. These are: (1) The conductance of the dielectric or leakage, (2) the earth capacitance, (3) the resistance of the leads, (4) the capacitance of the leads and (5) the inductance of the leads.

In the present work these sources of error were greatly reduced by the design of the apparatus, Fig. 1. The earth capacitance was very largely removed by the design of the measuring cell. Except for the small Bakelite insulator, the cell, Fig. 2, was constructed entirely of metal and provided with a water jacket for temperature control. During measurements the outer plate is connected to the ground and only the electric field through the insulator can cause an earth capacitance.

The errors due to resistance were practically eliminated by the use of heavy brass strips for all leads in the resonance circuit. The errors due to capacitance and inductance were reduced to a minimum by making the leads as short as possible, especially those connecting the cell and the precision condenser. Reference to Fig. 1 will indicate how these objectives have been attained.

By the substitution method used, the capacitance C_x^* is obtained as the difference in readings on the precision condenser at the resonance points when the measuring cell is in the circuit and when it is out. The differences are obtained by a method similar to that described by Malone.⁶

It was found that the apparent capacitance of the empty cell changes with wavelength, being noticeably larger at longer wavelengths. One might expect that the capacitance of the cell full of liquid would increase in approximately the

same ratio as that of the empty cell so that the relation $\epsilon' = C_x/C_s$ would be maintained. However, the dielectric constants calculated thus are too small indicating that the measured capacitance of the empty cell is too large. This is probably due to the unavoidable presence at some point, in any cell which might be used, of an insulating material having a greater dielectric constant than air, its relative effect being greater when the condenser is empty.

A test using benzene and carbon disulphide, however, showed that the relation

$$C_C/C_B = \epsilon_C'/\epsilon_B' = \text{a constant}$$

was independent of frequency. Here C_C and C_B are differences in condenser readings for carbon disulphide and benzene, non-polar liquids of known dielectric constants ϵ_C' and ϵ_B' , respectively. Since the dielectric constants measured in this work were intermediate between those of benzene and CS_2 , it was assumed that the relation would apply in all such measurements. As a generalized expression $\epsilon_x' = (C_x/C_B)\epsilon_B'$ was used for the unknown material. A further confirmation of this relation was later furnished by the fact that the dielectric constants of Sun Oil 30 calculated therefrom were constant throughout the wavelength range employed.

The values for ϵ' at the four intermediate wavelengths are plotted to scale against wavelength in Figs. 3-7. The values at the two extreme wavelengths spoken of earlier are also shown but are not plotted to scale horizontally. That these curves represent portions of true but not simple dispersion regions can be best shown by an analysis of a set of theoretical dispersion curves, Fig. 8. For curve *B* the assumed values were $\epsilon_0 = 2.46$, $\epsilon_\infty = 2.60$ and $\tau = (4/\pi) \times 10^{-6}$. Other necessary data appear on the figures. The effect of temperature, largely due to resulting changes in viscosity, is shown by a comparison of curves *A*, *B* and *C*. The density change with temperature is insignificant, but the change in viscosity η_i is very great if it is assumed that the temperature effect is roughly the same on microscopic as it is on macroscopic viscosity. The viscosity ratios $\eta_{50^\circ} : \eta_{25^\circ} : \eta_{18^\circ} = 0.1 : 1 : 2$ used for the curves are approximately those for the macroscopic viscosi-

⁶ Malone-Ferguson-Case, J. Chem. Phys. 1, 836 (1933).

⁷ R. Gunn, Phil. Mag. 48, 224 (1924).

⁸ Lattey-Gatty, Phil. Mag. 7, 985 (1929).

* Since the relation between capacitance and condenser readings is linear over the range employed, differences in readings were used in all calculations rather than actual capacitances.

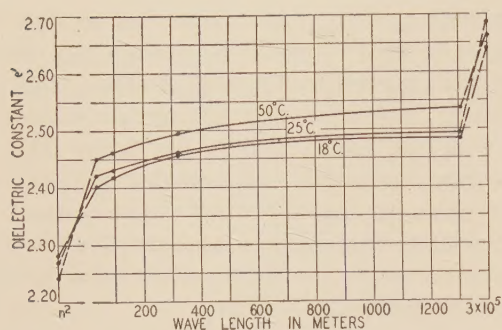


FIG. 3. Dispersion curves. Sun Oil 30 containing 10 percent lecithin.

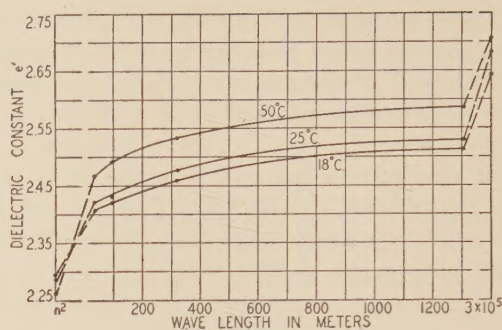


FIG. 6. Dispersion curves. Sun Oil 50 containing 10 percent lecithin.

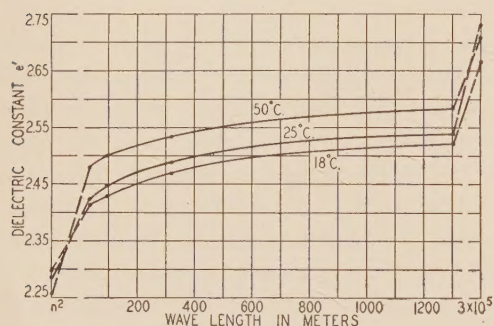


FIG. 4. Dispersion curves. Sun Oil 40 containing 10 percent lecithin.

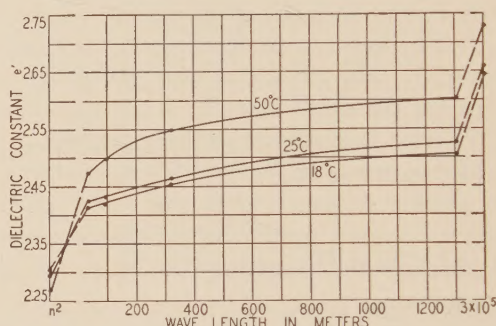


FIG. 7. Dispersion curves. Sun Oil 60 containing 10 percent lecithin.

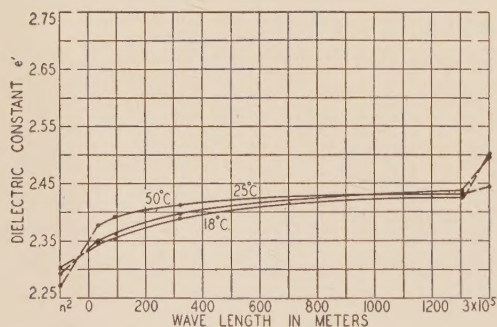


FIG. 5. Dispersion curves. Sun Oil 50 containing 3 percent lecithin.

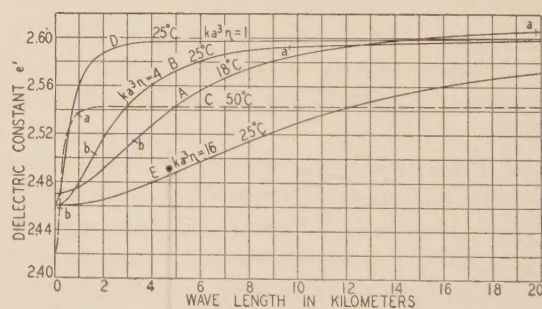


FIG. 8. Theoretical dispersion curves.

ties of Sun Oil 30. The values of ϵ_0 chosen were 2.47 at 18° and 2.42 at 50°. In obtaining these values it was assumed that the effect of temperature on ϵ_0 was the same as that measured for n^2 for the solutions.

Curves D, B and E show the effect of change in particle size or in viscosity at constant temperature. As seen in the figure the values of a^3 for these three curves are in the ratios of 1 : 4 : 16.

It will be seen that in the region of low wavelengths in all cases the values of ϵ' are small and approach ϵ_0 . In the high wavelength region the values of ϵ' are large and very rapidly become constant. In each of these regions the temperature coefficient of the dielectric constant is negative (curves A, B and C). However, in the region of dispersion the temperature coefficient is decidedly positive. Thus the general effect of in-

creasing the temperature is to shift the whole curve to somewhat lower values of dielectric constants and to considerably lower wavelengths. For instance, on curve *A*, by increasing temperature, the points (a) and (b) are shifted to the corresponding positions indicated on curves *B* and *C*. The effect of increasing either the size a^3 of the particles or the viscosity η , of the solvent is to shift the whole curve to higher wavelengths, as shown by curves *B*, *D* and *E*. In the light of these theoretical curves it can be shown that Figs. 3-7 represent the behavior of materials which are dispersing.

On examination of Figs. 3, 4, 6 and 7 it is seen that the temperature coefficient is always negative for the values of $\epsilon_0 = n^2$, while for the value ϵ' at wavelengths from 32.8 m to 1308 m it is positive in all cases. Thus there is a complete reversal of the magnitude of ϵ' with temperature. This is characteristic of the lower end of dispersion curves as will be seen in Fig. 8. Again, it is observed that the values of ϵ' for the two less viscous solutions (S. A. E. 30 and 40) at 1036 cycles (the extreme upper value) and 50° have dropped below the corresponding values at 25° and that while the corresponding value for the S. A. E. 50 solution has approached the value at 25°, it has not yet dropped below it. The corresponding value for S. A. E. 60 solution has maintained its relative position.

These reversals for the less viscous solutions would indicate that the values at 1036 cycles are either near or upon the upper plateau of the dispersion curves. From an examination of the theoretical curves, Fig. 8, it would be expected that the less viscous solutions at the highest temperatures would reach the top of the curve at lower wavelengths while the more viscous solutions would approach it at higher wavelengths. There is no indication in the range covered of the value at 25° on any of the curves tending to drop below that for 18°.

The apparent discrepancy in the height of corresponding curves for the different oils is due to the difference in the dielectric constants of the pure oils. When corrections for the latter are made the curves for the different solutions at the same temperature assume their expected relative positions. Furthermore, the magnitude of these shifts is of the right order since the change

in viscosity from one oil to the next is less than the change in viscosity of any one oil due to temperature in passing from 18° to 25°.

In Fig. 5 for the 3 percent solution, dispersion is shown even more definitely by the fact that the order is completely reversed not only between optical frequencies and 32.8 m but also at the other end of the curves. In fact, the curve for 50° begins to approach that for 25° between 200 and 300 m, crossing it at about 1000 m and falling much below even those for 18° at 1036 cycles (289,570 m).

The fact that the value of ϵ' at 25° has dropped below that for 18° at 1036 cycles indicates, also, that for this concentration dispersion occurs at lower wavelengths than for the higher concentration.

Since the temperatures are the same and the viscosities greater than those of the Sun Oil 30 and 40 solutions, the lowered dispersion range must be ascribed, in accordance with the Debye theory, at least, to the presence of smaller particles. This clearly indicates association of the lecithin molecules. These phenomena all indicate distinct dispersion, but it must be admitted that considering the rapid dispersion at low wavelengths the dispersion covers too great a range to be a simple dispersion region.

It becomes evident that it is desirable to obtain a larger number of points on the curve for one solution and to extend the measurements to longer wavelengths in order to determine the possibility of the presence of irregularities in the curve indicating the presence of simple overlapping dispersion curves.

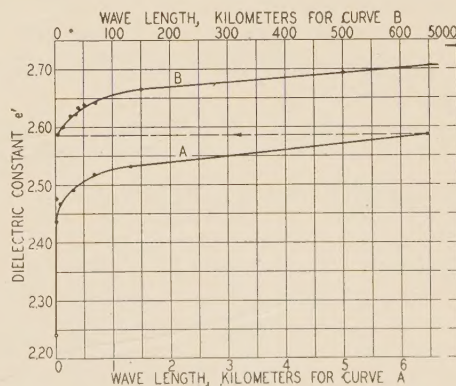


FIG. 9. Dispersion curve, Sun Oil 3 containing 10 percent lecithin, at 50°C.

The system used for this extended work was a solution containing 10 percent lecithin in Sun Oil 30 at 50°C. A set of measurements was made throughout the whole wavelength range on benzene and also on pure Sun Oil 30. The value at all frequencies for Sun Oil 30 was 2.293 ± 0.003 .

The curve of Fig. 9 is a plot of the data obtained.* Curve *B* represents the entire range of wavelengths down to 6450 m while curve *A* shows the lower portion from 6450 m to zero meters expanded horizontally 100-fold.

Even with these more extensive and precise data no evidence is obtained of separate dispersion regions. As a matter of fact, except for the two extreme points at zero and infinite wavelengths the dielectric constant is found to be, within experimental error, a linear function of the logarithm of the wavelength and is represented by

$$\epsilon' = 2.324 + 0.0619 \log \lambda.$$

When the complex nature of the systems is considered the absence of the appearance of single dispersion regions is not surprising. Any one of the oils is doubtless a complex mixture of molecules of various sizes. The viscosity of each individual component is probably different and thus the relaxation time of a given polar molecule caused by each would be different. The resulting dispersion curve would therefore be a summation of several simple dispersion regions.

It has been suggested by Race¹⁰ and by Luthi⁵ that polar radicals within the molecule as well as the molecule as a whole might cause dispersion. Lecithin is supposed to consist of several long chain compounds joined together in one large molecule. The molecule as a whole would cease to orient at very long wavelengths, and the various radicals would cease with frequency in

the order of their size, each having a different relaxation time. This likewise would result in a complex dispersion curve. Either or both of these explanations could account for the lower portion of the dispersion curves obtained.

The upper portions of the complex dispersion curves may be caused by the presence of associated groups of different sizes. It was shown in the discussion of Fig. 5 that lecithin is highly associated. These associated particles might readily approach colloidal dimensions and thus possess long relaxation periods.*

Recently several other investigators have obtained dispersion curves which failed to show discrete dispersion regions. Among these may be mentioned Kitchin,¹¹ Race¹⁰ and Williams¹² each of whom experienced difficulty in the interpretation of the data obtained in terms of the Debye theory. In some cases the difficulty doubtless would have been enhanced if a wider frequency range had been covered. Williams states "In conclusion, it may be said that these results show that the Debye theory, although theoretically sound, is very difficult to apply quantitatively to the existing dielectric constant data. . . . At the present time it does not seem readily possible to obtain monodisperse systems either of large molecules or of particles of colloidal size, in non-polar solvents."

Among the unique features of the present investigation are: (1) The design and assembly of the cell and receiver to minimize various errors present in such measurements, (2) the large number and extremely wide range of wavelengths employed, (3) the type of solute-solvent system employed, and (4) the relatively large change of dielectric constant with frequency for such viscous solutions.

* The value at 39.2 m is obviously in error, but circumstances made it impossible to recheck it after plotting the curve.

¹⁰ H. H. Race, *J. Phys. Chem.* **36**, 1928 (1932).

* An approximate calculation shows that associated particles of about 1000 molecules are sufficient to account for the dispersion at the upper end of the curve.

¹¹ D. W. Kitchin, *J. Ind. and Eng. Chem.* **24**, 549 (1932).

¹² Oncley-Williams, *Phys. Rev.* **43**, 341 (1933).

